



The preparation and characterization of bismuth thin films on GaSb(110) using low energy electron diffraction  
by Scott Len Lantz

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in  
Physics  
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Abstract:

The growth of thin bismuth films on the GaSb(110) surface has been studied using low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The GaSb samples were single crystal bars and the (110) surface was prepared by cleaving in situ. Bismuth was evaporated from a solid source, and the evaporation was monitored with a quartz crystal oscillator. Diffraction spot profiles and integrated intensity versus voltage (IV) curves were measured at temperatures ranging from 120 K to 350 C. Bismuth was found to grow epitaxially for monolayer coverages, preserving the  $p(1 \times 1)$  LEED pattern symmetry. Upon annealing a phase transition occurred such that the  $p(1 \times 1)$  symmetry was replaced by a  $p(1 \times 2)$  symmetry, where the LEED pattern periodicity was doubled along the [001] direction of the bulk GaSb crystal. Preliminary work has been done toward the determination of the atomic structure of the Bi/GaSb(110) interface. Modifications were made to the existing computer programs, including the incorporation of the simplex algorithm into the structure search decision-making process. Using this method, the calculated atomic structure of the clean GaSb(110) surface was shown to be in agreement with that obtained by previous methods. Searches were also made for the atomic structure of the  $p(1 \times 1)$  structure for a bismuth coverage of one monolayer. The results indicate an ordered bismuth overlayer with an atomic structure differing markedly from the truncated bulk or reconstructed clean GaSb(110) surface structure.

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APPROVAL

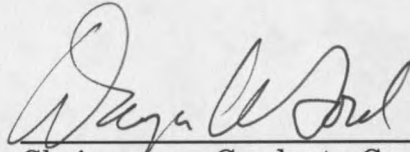
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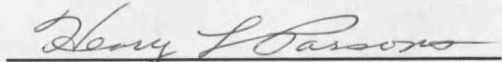


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## ABSTRACT

The growth of thin bismuth films on the GaSb(110) surface has been studied using low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The GaSb samples were single crystal bars and the (110) surface was prepared by cleaving *in situ*. Bismuth was evaporated from a solid source, and the evaporation was monitored with a quartz crystal oscillator. Diffraction spot profiles and integrated intensity versus voltage (IV) curves were measured at temperatures ranging from 120 K to 350 C. Bismuth was found to grow epitaxially for monolayer coverages, preserving the p(1x1) LEED pattern symmetry. Upon annealing a phase transition occurred such that the p(1x1) symmetry was replaced by a p(1x2) symmetry, where the LEED pattern periodicity was doubled along the [001] direction of the bulk GaSb crystal. Preliminary work has been done toward the determination of the atomic structure of the Bi/GaSb(110) interface. Modifications were made to the existing computer programs, including the incorporation of the *simplex algorithm* into the structure search decision-making process. Using this method, the calculated atomic structure of the clean GaSb(110) surface was shown to be in agreement with that obtained by previous methods. Searches were also made for the atomic structure of the p(1x1) structure for a bismuth coverage of one monolayer. The results indicate an ordered bismuth overlayer with an atomic structure differing markedly from the truncated bulk or reconstructed clean GaSb(110) surface structure.



## CHAPTER 1

## INTRODUCTION

The work presented in this thesis represents the results of the experimental and theoretical investigations into the growth of thin bismuth films on the GaSb(110) surface. The motivation for such a study is many-fold. GaSb (gallium antimonide) is an important III-V semiconductor. It has many industrial applications for the construction of electronic devices such as electro-optical sensors and light emitting diodes [1]. The successful construction of electronic devices, which are getting increasingly smaller, could benefit greatly from the knowledge of atomic and electronic structures of semiconductor-metal interfaces. This is important in studying the formation of Schottky barriers and ohmic contacts [2]. At the atomic scale, however, little is understood about the electronic structure at these interfaces, due to complex atomic reconstructions of the semiconductor substrate and lack of sufficient theoretical models to describe the interface [2]. Although the (110) surface of the III-V semiconductors is less used in industrial applications (than, for example the (100) surface), it is somewhat simpler in that the surface is charge-neutral, and the substrate reconstructions are comparatively well understood [2,3]. Clean (110) surfaces hence provide an excellent basis for the study of atomic and electronic structures at metal interfaces.

Bismuth was selected as an adsorbate because it was found to form an ordered interface on a similar III-V compound GaAs(110) [4]. For this reason it

was believed that bismuth would form an ordered interface on GaSb(110), which could then be studied by LEED (low energy electron diffraction), which is a powerful and extensively-used tool for surface analysis.

The experimental techniques used in the study of the Bi/GaSb(110) system include LEED and AES (Auger electron spectroscopy). The growth of bismuth was investigated for monolayer coverages, and the effects of annealing were studied. Measurements taken with LEED included diffraction spot intensity profiles and intensity versus voltage (IV) curves. Auger measurements were primarily used to measure the desorption of bismuth that occurred when the sample was annealed.

The theoretical analysis of the data involved modelling of the atomic structure of the interface. This included dynamical LEED calculations for the generation of IV data for the proposed model, which could then be compared to the experimental IV data. A best fit structural model was then searched for by making changes to the model until the calculated data best matched the experimental data. In the following chapters, the results of these studies of the Bi/GaSb(110) system are presented following a description of the techniques used.

## CHAPTER 2

## CONCEPTS IN LEED CRYSTALLOGRAPHY

The LEED Experiment

The essential elements of a LEED apparatus consist of an ultra-high vacuum chamber, an electron gun to provide a monoenergetic electron beam over an energy range from 30 to 400 eV, a crystal holder with facilities for moving, heating and cooling the sample, and a detection system for measuring the number of elastically scattered electrons in a prescribed direction. The type of detection system used in this work is the display system shown schematically in Figure 1.

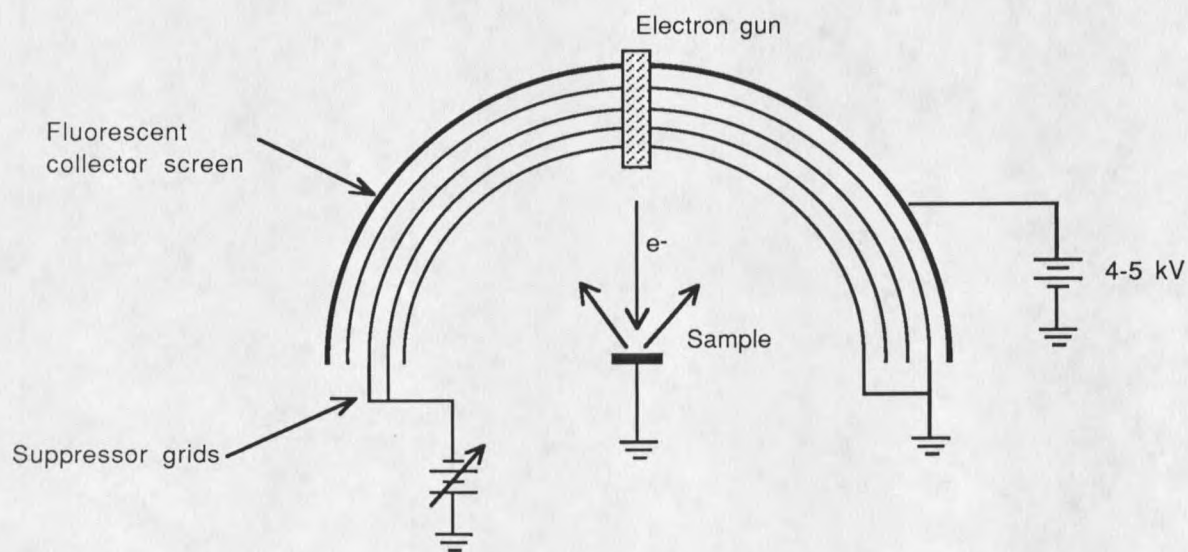


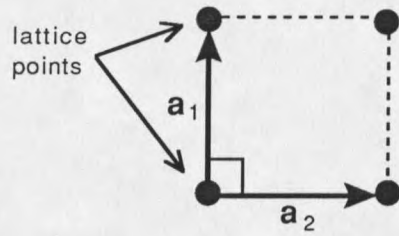
Figure 1: Display detection system for LEED

The electron gun produces a beam of electrons which scatter from the crystal surface. The elastically scattered electrons are filtered by the suppressor grids, then accelerated into the fluorescent screen by a voltage of 4-5 kV. The intensity pattern produced by the electrons striking the screen can then be measured by photographic or video recording techniques. For a well-ordered crystal surface, the LEED intensity pattern contains a wealth of information concerning the surface symmetries and surface atomic geometries. The extraction of these surface properties, though, often requires extensive analyses. The notation and methods used in such analyses are developed below.

### Surface Classifications

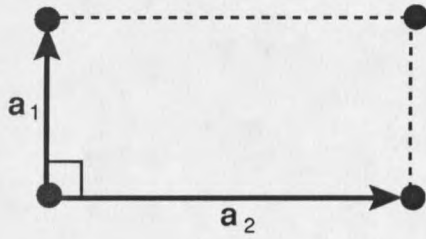
When considering an ordered surface, there are two important fundamental concepts, that of a lattice and a basis. The lattice is the two dimensional array of reference points which possess the translational symmetries of the surface. The basis is the arrangement of the surface atoms with respect to the lattice points. The geometry of a particular surface structure is said to be completely determined once both the lattice and the basis are known. There are five possible distinct two dimensional lattices, called Bravais lattices. These are shown in Figure 2. The primitive vectors,  $\mathbf{a}_1$  and  $\mathbf{a}_2$ , define the surface unit cell, and are generally selected to form the smallest possible parallelogram which preserves the surface symmetries.

The classification of a surface structure often relates the two dimensional surface lattice to the three dimensional substrate lattice. One scheme, proposed by Park and Madden [5], relates the surface lattice primitive vectors ( $\mathbf{a}_1, \mathbf{a}_2$ ) to



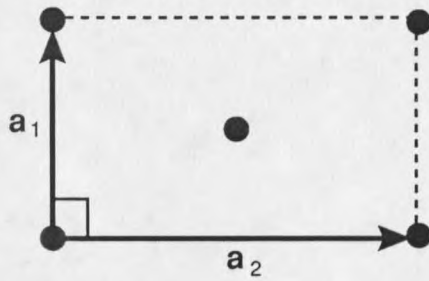
**Square**

$$a_1 = a_2$$



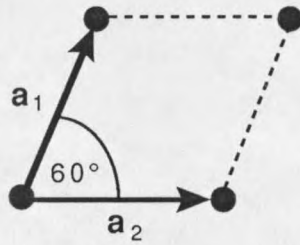
**Primitive Rectangular**

$$a_1 \neq a_2$$



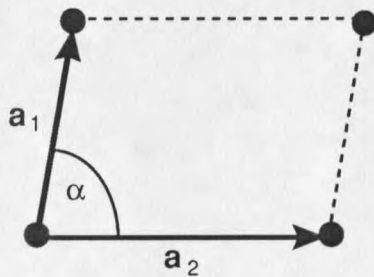
**Centered Rectangular**

$$a_1 \neq a_2$$



**Hexagonal**

$$a_1 = a_2$$



**Oblique**

$$a_1 \neq a_2$$

$$\alpha \neq 90^\circ$$

Figure 2: Two-dimensional Bravais lattices

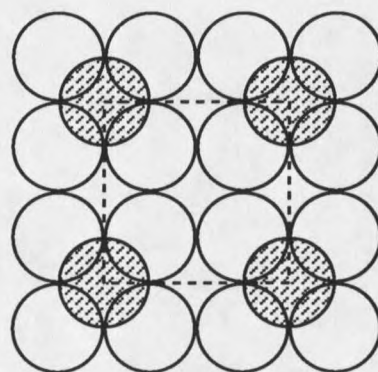
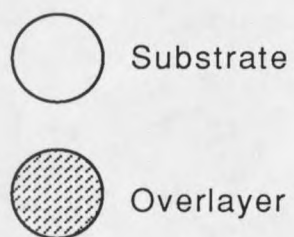
those of a parallel substrate plane ( $\mathbf{b}_1, \mathbf{b}_2$ ) with a transformation matrix  $\mathbf{M}$ , such that

$$\begin{aligned}\mathbf{b}_1 &= M_{11}\mathbf{a}_1 + M_{12}\mathbf{a}_2 \\ \mathbf{b}_2 &= M_{21}\mathbf{a}_1 + M_{22}\mathbf{a}_2\end{aligned}\tag{1}$$

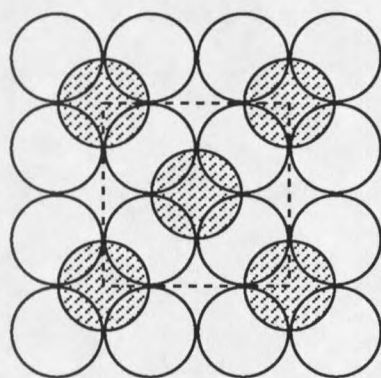
The structure is called simple when all entries of  $\mathbf{M}$  are integers, and coincidental if  $\mathbf{M}$  contains both integers and rational numbers. If  $\mathbf{M}$  contains irrational numbers, the structure is labelled incoherent or incommensurate. Although universally applicable, this method does not always provide an intuitive picture for what the structure looks like. Other methods have been proposed which are more descriptive, such as the one proposed by Wood [6]. Here, the relation between the surface and substrate lattices is expressed by the ratios of the lengths of the primitive vectors,  $|\mathbf{b}_1/\mathbf{a}_1|$  and  $|\mathbf{b}_2/\mathbf{a}_2|$ , and the rotation angle between the two lattices,  $\phi$ . The surface unit cell is labelled as either centered (c), or primitive (p). A centered unit cell implies that there is a lattice point in the center of the surface unit cell. This method is simple and applicable to a large number of structures, including the Bi/GaSb(110) system studied here. Some examples of labelling with this scheme are presented in Figure 3.

Directions on the surface are usually expressed in relation to the unit cell. A standard approach is to use the Miller indices  $h'$  and  $k'$ , where  $h'$  and  $k'$  are both integers, such that  $(h', k')$  refers to a direction on the surface. This direction is defined to be perpendicular to the translation vector  $\mathbf{D}$  given by

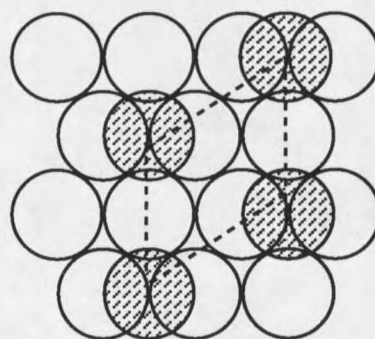
$$\mathbf{D} = h'\mathbf{a}_1 + k'\mathbf{a}_2\tag{2}$$



$p(2 \times 2)$



$c(2 \times 2)$



$p(\sqrt{3} \times \sqrt{3}) 30^\circ$

Figure 3: Examples of surface classifications

As illustrated in Figure 4, the surface lattice can be thought of as parallel rows of points with separation  $d_{h'k'}$  given by

$$\frac{1}{d_{h'k'}^2} = \frac{h'^2}{a_1^2 \sin^2 \gamma} + \frac{k'^2}{a_2^2 \sin^2 \gamma} - \frac{2h'k' \cos \gamma}{a_1 a_2 \sin^2 \gamma} \quad (3)$$

where  $\gamma$  is the angle between  $\mathbf{a}_1$  and  $\mathbf{a}_2$ . This interpretation will become useful in the next section in discussing the geometric theory of diffraction.

### Geometric Theory of Diffraction

The starting point for describing electron diffraction at crystal surfaces is the de Broglie relation,

$$\lambda = h/p \quad (4)$$

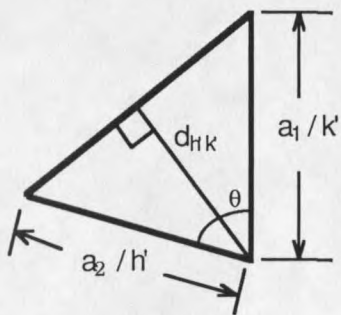
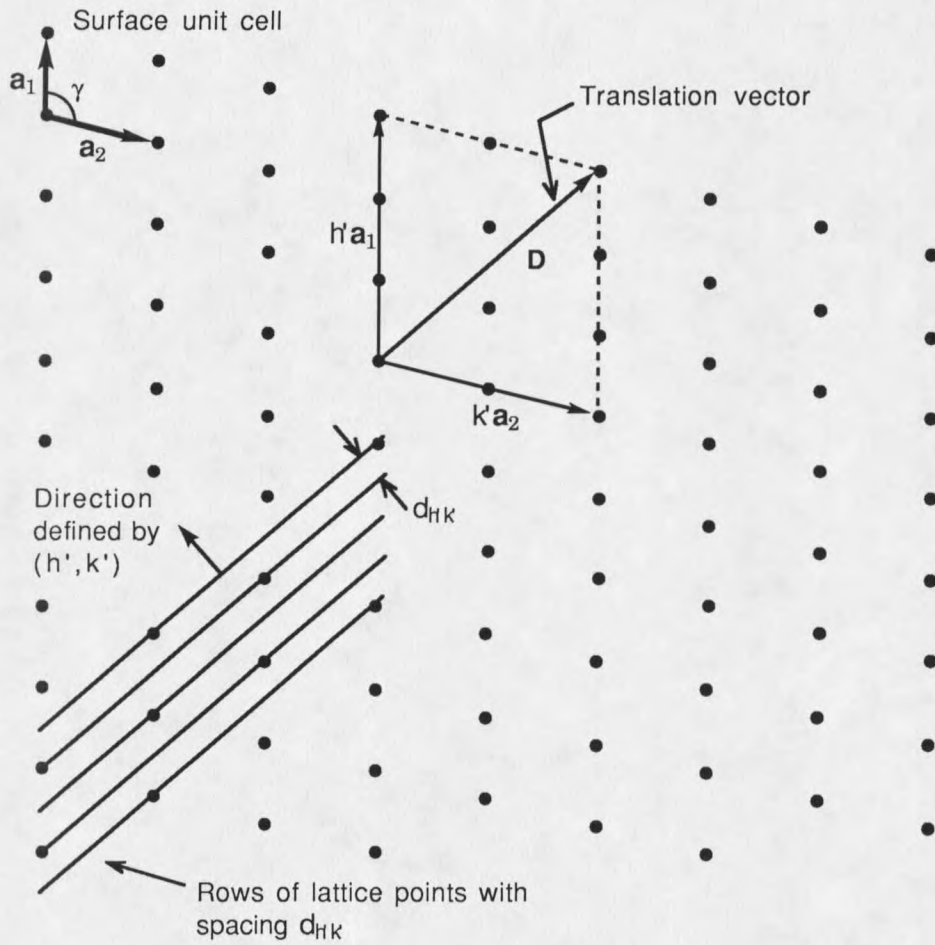
which relates the linear momentum of the electron  $p$  to its wavelength  $\lambda$ .  $h$  is Planck's constant ( $4.13 \times 10^{-15}$  eV sec). When expressed in terms of the kinetic energy of the electron ( $E = p^2/2m$ ), the de Broglie relation becomes

$$\lambda = h/\sqrt{2mE} \quad (5)$$

When  $\lambda$  is in Angstroms ( $\text{\AA}$ ), and the energy  $E$  is in electron volts (eV), the relation is approximately,

$$\lambda \cong \sqrt{150/E} \quad (6)$$





$$\theta = \pi - \gamma$$

$$\frac{1}{d_{HK}^2} = \frac{h^2}{a_1^2 \sin^2 \gamma} + \frac{k^2}{a_2^2 \sin^2 \gamma} - \frac{2hk \cos \gamma}{a_1 a_2 \sin^2 \gamma}$$

Figure 4: Row representation of surface lattice points

Interference effects occur when the electron wavelength is of the same order of magnitude as the atomic spacing on the crystal surface. With atomic spacings on the order of a few Angstroms, the corresponding energy range is 1 to 500 eV. The actual energy range used in LEED experiments is somewhat smaller, 50-300 eV, owing to inelastic scattering and instrumental effects, which are discussed in later sections. In the geometric theory, all scattering is assumed to be elastic, and instrumental effects are ignored.

For elastic wave scattering from a one dimensional periodic array, constructive interference takes place when the scattered waves from neighboring lattice points have path differences of multiples of the electron wavelength  $\lambda$ . If  $d$  is the array spacing, and  $\theta_0$  is the angle of incidence measured from the normal, then constructive interference of the back-scattered waves occurs at angles  $\theta$  when,

$$d(\sin\theta - \sin\theta_0) = n \lambda \quad (7)$$

Here  $n$  is an integer denoting the order of diffraction. This is known as the Bragg equation in one dimension. Since our LEED experiments are performed at normal incidence, it will be assumed that  $\theta_0 = 0$ , henceforth.

In extending the Bragg equation to a two dimensional surface, recall from the previous section that the surface lattice points can be thought of as an ensemble of parallel rows with direction  $(h',k')$  and separation  $d_{h'k'}$ . When each row is considered a scatterer, interference maxima are expected for

$$\sin\theta = (1/d_{h'k'}) n \lambda \quad (8)$$

or with the use of equation (6),

$$\sin\theta = (1/d_{h'k'}) \cdot n \cdot \sqrt{150/E} \quad (9)$$

From this equation, it is evident that an increase in electron energy will cause the diffraction maxima to move closer to the surface normal, and that the larger the unit cell, the closer the first maximum will be to the surface normal.

In labelling the diffraction maxima, the Miller indices are combined with the order of diffraction  $n$ , to yield the Laue indices,

$$h = n h' \quad \text{and} \quad k = n k' \quad (10)$$

With this notation, a diffraction maximum is referred to as the  $(h,k)$  beam.

With most LEED apparatus, the diffraction beam pattern is directly observable, which in principle allows for the determination of  $d_{h'k'}$  and consequently the geometry of the surface unit cell. A more sophisticated approach to analyzing and interpreting LEED patterns makes use of the reciprocal lattice, described below.

For every two dimensional Bravais lattice, there exists a corresponding reciprocal lattice whose primitive vectors,  $(\mathbf{a}_1^*, \mathbf{a}_2^*)$  satisfy

$$\mathbf{a}_i \cdot \mathbf{a}_j^* = 2\pi\delta_{ij} \quad (11)$$

From this equation, the lengths and directions of the reciprocal lattice vectors can be determined.

$$a_i^* = \frac{2\pi}{a_i \sin \gamma} \quad \text{and} \quad (12)$$

$$\mathbf{a}_i^* \perp \mathbf{a}_j \quad \text{for } i \neq j \quad (13)$$

Here again  $\gamma$  is the angle between  $\mathbf{a}_1$  and  $\mathbf{a}_2$ . Reciprocal lattices for the five two dimensional Bravais lattices are shown in Figure 5. The utility of reciprocal space analyses is that the LEED pattern is a direct representation of the reciprocal lattice, as shown below.

The formation of the LEED pattern can be explained using the concept of reciprocal space with the help of an Ewald construction, shown for normal incidence in Figure 6. A set of lines is drawn perpendicular to the surface through the reciprocal lattice points, which become the reciprocal lattice rods. A sphere of radius  $1/\lambda$  is then drawn directly above one of the reciprocal lattice points at a distance  $1/\lambda$  from the surface. An arrow drawn from the center of the sphere to the surface represents the incident electron wave vector. The intersections of the reciprocal lattice rods with the sphere define the directions of the diffraction beams. The vectors  $\mathbf{k}_0$  and  $\mathbf{k}$  represent the wave vectors of the incident and scattered beams, respectively, and  $\mathbf{k} - \mathbf{k}_0$  is the momentum transfer. It can be seen from this construction that the diffraction beams completely characterize the symmetries of the reciprocal lattice, so the LEED pattern is a direct representation of the lattice.

Once the reciprocal lattice of a surface structure is determined (from the LEED pattern), the Bravais lattice can be found by a transformation from

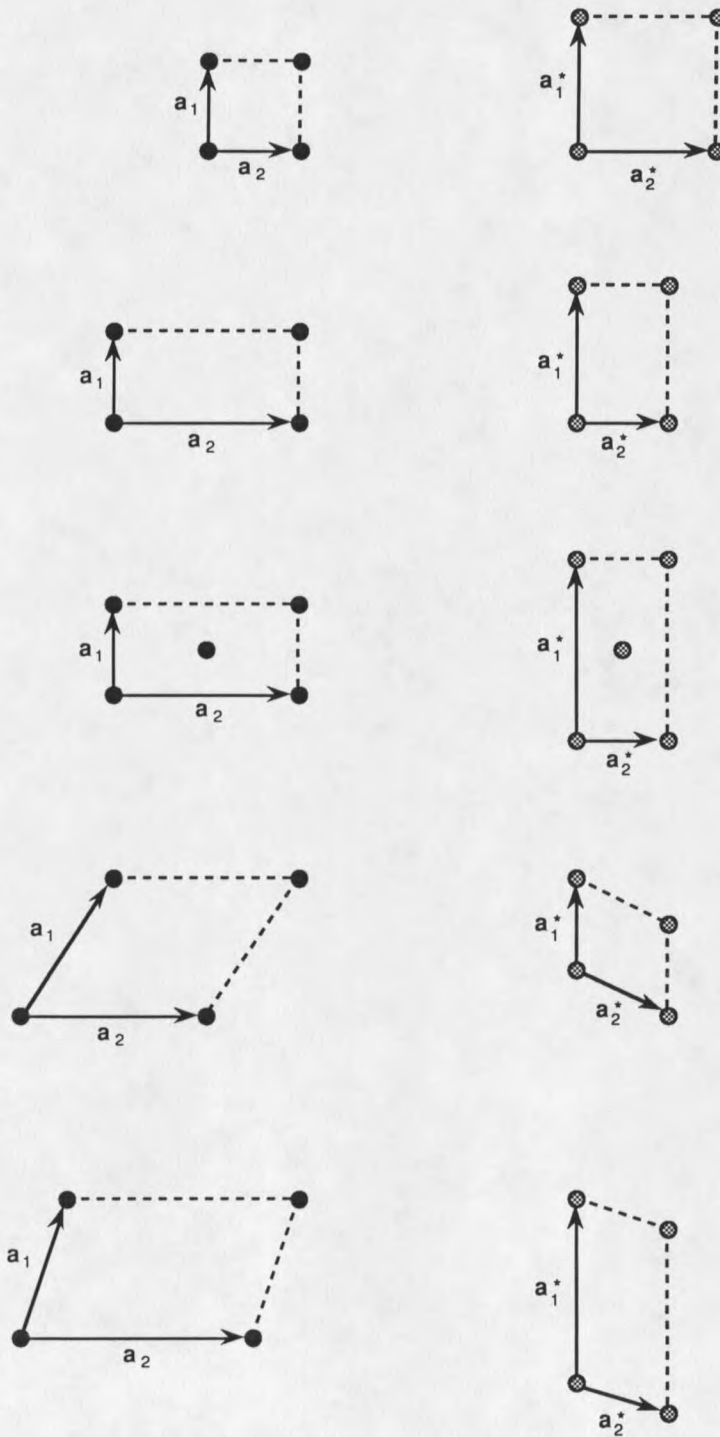
Real Space LatticeReciprocal Space Lattice

Figure 5: Two-dimensional reciprocal lattices

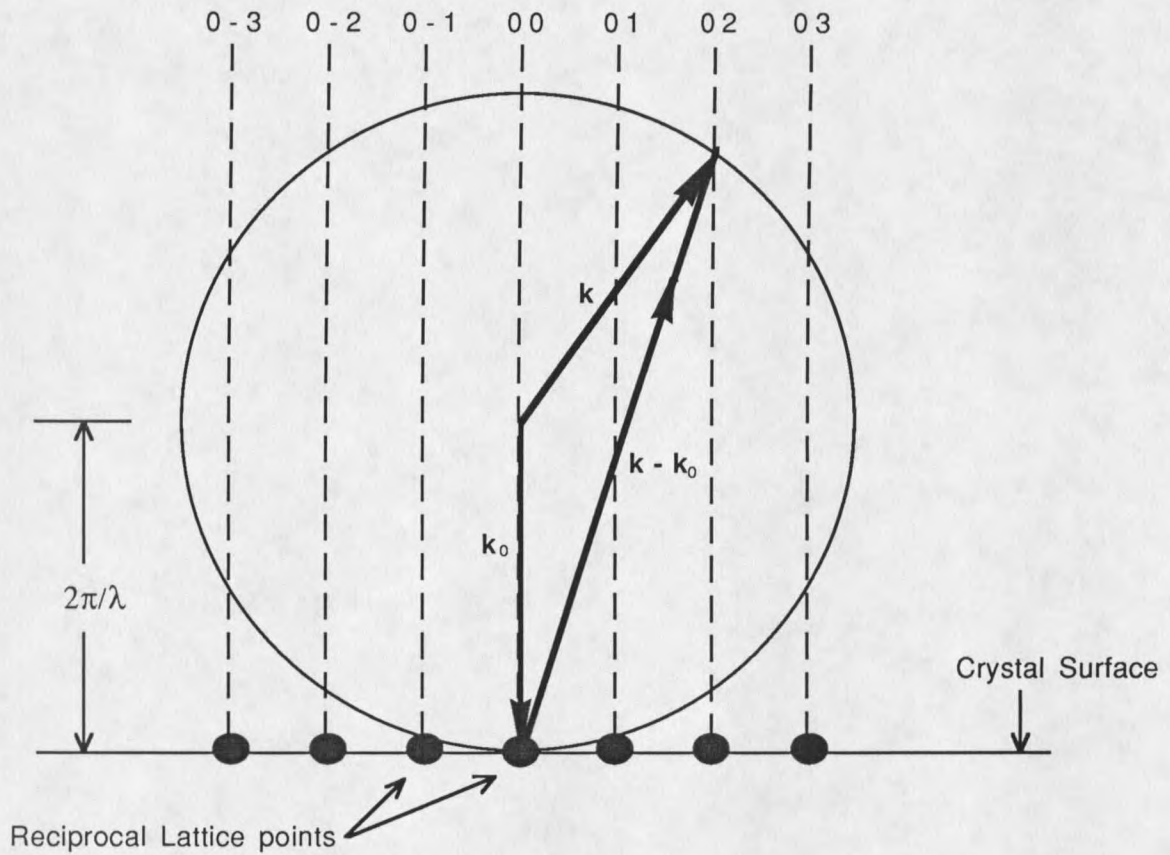


Figure 6: Ewald Construction

reciprocal space to real space. The surface reciprocal lattice,  $(\mathbf{a}_1^*, \mathbf{a}_2^*)$  may be correlated to that of the substrate,  $(\mathbf{b}_1^*, \mathbf{b}_2^*)$  in a manner similar to equation (1).

$$\begin{aligned} \mathbf{b}_1^* &= M_{11}^* \mathbf{a}_1^* + M_{12}^* \mathbf{a}_2^* \\ \mathbf{b}_2^* &= M_{21}^* \mathbf{a}_1^* + M_{22}^* \mathbf{a}_2^* \end{aligned} \quad (14)$$

The  $M_{ij}^*$  can be determined by an inspection of the LEED pattern. The transformation to find the matrix  $M$ , from  $M^*$  is [7]

$$M_{ij} = \left( \frac{\pm 1}{\det \mathbf{M}^*} \right) \cdot M_{ji}^* \quad (15)$$

The advantages of using reciprocal lattices in LEED pattern analysis becomes more evident when studying overlayer structures and patterns with domains. Detailed descriptions of these types of analyses are discussed in references [7,8].

So far only the positions of the diffraction beams have been considered. Analysis of the beam positions can be used to determine the geometry of the surface unit cell, but provides no information for the atomic positions within the unit cell, i.e. the basis. This information is contained in the diffraction beam intensities. The diffraction beam intensity as a function of electron energy is very sensitive to atomic positions, and thus provides a means of deducing the complete atomic geometry. There does not exist, however, a means of extracting a geometry directly from the IV curves. The most common approach is to employ a search technique, whereby calculated IV curves for a proposed theoretical model are compared to the experimentally obtained curves, then changes are made to the model until the two sets of IV curves are compatible. The techniques for structure searches are discussed further in Chapter 5. In the following section the basic elements for a kinematical theory of scattering are discussed, then some development is made toward describing a more complete dynamical theory.

### Diffraction Intensities

The determination of the basis for a surface structure relies on the analysis of the diffraction intensities and their dependence on the incident electron energy. I present below a kinematical development, in which the effects of multiple scattering and inelastic scattering are ignored. Extensions to more complete dynamical theories which include these effects are then discussed. The















































































































































